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## (54) METHOD FOR MANUFACTURING MEMBRANE AND FINE STRUCTURE, AND FINE STRUCTURE

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing a membrane uniform in thickness and composition on a substrate without relying on a combination of a solute and a solvent.

SOLUTION: In the method for forming the membrane such as a transparent electrode film or the like on the substrate, when a solution for forming the membrane is adapted to the substrate to be formed into the membrane, the substrate is placed under rapid pressure reducing environment.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** An electron device, the device for a display, etc. are further related [ the thin-film-fabrication approach which makes it the content for this invention to form a thin film in a substrate, the manufacture approach of the fine structure object which equipped the substrate with the thin film, and ] especially with a substrate about the fine structure object at a thin film and the fine structure object with which it comes to form the pattern further.

**[0002]**

**[Description of the Prior Art]** Conventionally, the approach which used the approach and ink regurgitation equipment by the photolithography as the approach of patterning of a thin film exists. To the former approach having a complicated process, the latter approach is easy, and since it is low cost, it attracts attention recently.

**[0003]** As an example of the fine structure object manufactured using the latter approach, an organic electroluminescence (electro RUMINESSESU (it is described as organic electroluminescence below)) display exists. In order to manufacture the fine structure object concerning an organic electroluminescence display, using luminescent material, such as an organic fluorescence ingredient, as ink with a solvent, and carrying out the regurgitation of this ink to a substrate according to a luminescence pattern from ink regurgitation equipment is performed. The organic electroluminescence display is equipped with the structure where the above-mentioned organic luminescent material has been arranged between an anode plate and cathode for every pixel. In detail, first, a fluorescence ingredient is dissolved in a suitable solvent and ink is obtained. The regurgitation of this ink constituent is carried out so that the transparent electrode on the base material with a transparent electrode as an anode plate of EL display may be covered. Subsequently, after carrying out desiccation clearance of the solvent to ink and forming a luminescent-material layer, on this luminescent-material layer, metals, such as small calcium of a work function and magnesium, are made to deposit by approaches, such as vacuum evaporation and a spatter, and cathode is formed. The layer of a luminescent material as stated above can be prepared between an anode plate and cathode by carrying out like this.

**[0004]** By the ink jet regurgitation method, there are a methanol, water, etc. as a solvent of ink. Although the functional material of a low-molecular system or the functional material of a macromolecule system is used as a luminescent material, there are some which are not fully dissolved in a solvent depending on luminescent material. Therefore, a solvent dries, or luminescent material deposits, blinding occurs on the head of the ink regurgitation, or there are problems -- the film of a homogeneous luminescent material is not obtained. For this reason, heating ink at the time of the ink regurgitation, or heating a substrate is proposed.

**[0005]**

**[Problem(s) to be Solved by the Invention]** However, when heating a substrate, in order for the viscosity of the ink constituent breathed out by the substrate to fall, the approach for attaining more uniform thickness is required. To use the technique which was excellent in control of the film-izing especially

with the ink regurgitation method in the minute drop applied to the substrate is desired.

[0006] Then, this invention aims at offering a solute and how it is not based on the combination of a solvent but thickness and a presentation manufacture a uniform thin film on a substrate. Other objects of this invention are offering the manufacture approach of a fine structure object of coming to form the above-mentioned thin film in a substrate. The object of further others of this invention is offering the fine structure object with which it comes to form the above-mentioned thin film in a substrate.

[0007]

[Means for Solving the Problem] In order to attain this object, in case this invention applies the solution for forming said thin film to this substrate in the approach of forming a thin film in a substrate and filmizes this solution, it is characterized by putting said substrate on the bottom of a rapid reduced pressure environment.

[0008] In this invention, the pressure which it is going to use an ingredient as the film, without changing the viscosity of the solution for removing a solvent and forming a thin film, without heating a substrate substantially, the parameter of temperature was not changed, and the substrate has set is changed, and a functional thin film is formed. In order to secure the uniformity of this thickness, the momentary dissolution clearance by the rapid pressure variation which is in the condition of not balancing was used for membrane formation. In this invention, a rapid reduced pressure condition means the environment where such pressure variation can be realized.

[0009] When said solution is the minute drop breathed out by the substrate by the ink regurgitation approach, the effectiveness of equalization of the thickness obtained with reduced pressure is more remarkable in the operation gestalt of this invention. Although said substrate is then put under reduced pressure, without heating from a room temperature, in a room temperature, it does not decompress below to the vapor pressure of the solvent of a solution. When freezing of said solution arises especially with reduced pressure, it is desirable to carry out temperature up of the substrate gradually, and to perform film-ization of the solution concerned.

[0010] In case this invention applies the solution for forming said thin film in a substrate in the manufacture approach of a fine structure object of coming to form a thin film in a substrate to this substrate and film-izes this solution in order that it may attain said object and, it is characterized by putting said substrate on the bottom of a rapid reduced pressure environment.

[0011] In the fine structure object with which, as for this invention, a substrate comes to form a thin film further, in case that of said thin film applies the solution for forming this thin film to this substrate and film-izes this solution, it is characterized by being the fine structure object which it comes to form by having put said substrate on the bottom of a rapid reduced pressure environment.

[0012] The manufacture approach of the thin film concerning this invention is applicable to formation of the thin film of formation and the other electron devices of the luminous layer in EL indicating equipment which it was widely applied to the approach of supplying a minute quantity of a solution on a substrate, for example, was mentioned above, and a pan at the metal thin film of an indicating equipment.

[0013] The fine structure object of this invention means the substrate with which metal circuit patterns, such as a substrate which says on a substrate a thin film and the thing in which especially the pattern is formed, for example, is used with various electronic device, electron devices, etc., a substrate with which the organic electroluminescence layer of the previous statement in a display device was formed in more detail, a light filter of a color liquid crystal display, and a semiconductor device, were formed. If the thickness of a thin film equalizes, in the case of a display device (for example, EL display), a uniform luminescence property can be demonstrated within a pixel. Moreover, in being electron devices, such as a semi-conductor, a thin film demonstrates a uniform electrical property.

[0014] The functional thin film which can realize the various functions in an organic electroluminescence indicating equipment, an electron device, etc. is contained in the thin film of this invention. What was specified in the vocabulary in which the thin layer, the functional thin layer, and the functional coat differed from the functional film etc. is included by the "thin film" of this invention.

[0015]

[Embodiment of the Invention] A drawing is used for below and the operation gestalt of this invention is explained to it. Specifically, the case where the formation approach of the thin film of this invention is applied to formation of the luminous layer of an organic electroluminescence display is shown. Drawing 1 is the perspective view of the organic electroluminescence display with which this invention is applied. The ITO electrode 3 as an anode plate is formed on the glass substrate 2. Moreover, the black matrix serves as a pattern of the bank (bank) 4 of the shape of two or more rectangle. Red, blue, and an organic green fluorescence ingredient are supplied to opening between this bank from the ink jet printer head 1.

[0016] The ITO electrode is formed by the dot-like pattern, and forms and drives the pixel respectively connected to the thin film transistor (TFT component) independently. Said bank for classifying each pixel is formed in the boundary of each pixel. The organic electroluminescence material (ink constituent) 5 breathed out from the ink jet recording head is supplied on the ITO electrode divided by the bank, and adheres to this.

[0017] First, the following luminescent material is blended to a solvent as an ink constituent. Although suitably chosen about the presentation of luminescent material and a solvent according to the luminescent color, dodecylbenzene, cyclohexylbenzene, a 1.2.3.4-tetramethyl benzene tetralin, diethylbenzene, a mesitylene, etc. can be used as a solvent, for example, using a fluorene system giant molecule and a giant molecule PPV as a solute. The concentration of a solute is 0.1 - 2.0wt%.

[0018] Subsequently, the regurgitation of the ink constituent is carried out to the dot pattern of ITO using an ink jet printer. Subsequently, in the state of a room temperature, EL light emitting device of drawing 1 is put into a decompression device, and is decompressed the following condition. Moreover, the example of a condition at the time of an ink jet printer activity is as follows.

[0019] Substrate temperature at the time of the regurgitation is made into 10-25 degrees C, it is desirable to hold humidity to 20% or less, and it sets discharge quantity per dot to 20pl.

[0020] Subsequently, in order to film-ize the minute drop of the ink constituent put on the dot pattern of ITO, a substrate is set by the reduced pressure environment with the rapid bottom of a room temperature. Here, generally a "room temperature" is 10-25 degrees C.

[0021] The reduced pressure environment is made into the pressure environment higher than the vapor pressure at the event of the solvent used for the solution for thin film formation as stated above. It is because it is suitable when real \*\* does not happen but a thin film is made into uniform thickness.

Although a pressure [ \*\*\*\* ] changes with solvents, it is desirable to consider as an about 1.5 times [ of vapor pressure ] pressure. Moreover, by this pressure, hold a substrate for 0.5 - 5 minutes, a solvent is made to remove, and a film is produced.

[0022] As for the time of concentration to place constant pressure, it is desirable that it is 20 or less seconds, and it is still more desirable to decompress by the time of concentration for 10 or less seconds.

[0023] In order to put a substrate on the bottom of a reduced pressure environment, it is based on what the solution for thin film formation puts the substrate by which coating was carried out into the chamber which can be sealed, and decompresses the inside of a chamber for. When freezing of a solvent arises with reduced pressure, a freezing condition is canceled by carrying out temperature up gradually by the programming rate 1 thru/or 5 degrees C / min [ near the melting point ]. A thin film with uniform thickness (luminous layer) can be obtained through the above process. It is flat and it is desirable for a part to mean the condition which is not a concave in the cross-section configuration of a thin film as the thickness of a thin film is almost uniform that there is no dispersion in thickness, and to fit in the range whose difference of the part where thickness is the thickest, and the part where thickness is the thinnest is 10%. In addition, after an ink constituent is supplied in the field divided by the bank and film-izes in this way, the cathode which becomes the upper layer from metals, such as magnesium and aluminum, further is formed, and an organic electroluminescence display is completed.

[0024] The thickness with a suitable thin film is about 0.1 micrometers, if it is an above-mentioned luminous layer, although it changes with applications, and if it is wiring, it is about 1 micrometer. In addition, when forming metal wiring of a semiconductor device, the colloidal solution which contains metals, such as gold and silver, as a solute so that the concentration of a solute may become 1 - 30wt%

is used as an ink constituent. This colloidal solution is making water mix and distribute said metal and macromolecule protective agents, such as a citric acid and Pori (n vinyl-2-pyrrolidone). This ink is produced under reduced pressure using ink jet printer equipment as discharge and the above-mentioned approach. Then, by irradiating light, macromolecule protective agent clearance is carried out and a flow is obtained.

[0025]

[Example] Hereafter, although this invention is explained still more concretely with reference to an example, this invention is not restricted to these.

[0026] [Example 1] To the substrate shown in drawing 1, with the application of the solution, the luminous layer was formed according to the following process, and the organic electroluminescence display was produced. Discharge application of the polymer solution whose concentration of a solute is 1wt% was carried out at the pixel pattern of ITO divided by the bank by the ink jet printer head, using dodecylbenzene as a solvent, using the poly fluorene as a solute. EL display device was obtained. Subsequently, EL display device in which the poly fluorene thin film luminous layer with a thickness of 1000A was formed was obtained by putting in in a chamber the substrate with which the solution was applied, and decompressing in 5 seconds from ordinary pressure to 10-2torr (1.3Pa) at a room temperature (20 degrees C).

[0027] The head of a trade name "MJ930C" was used for the ink jet method, and it performed the regurgitation conditions of a polymer solution as discharge quantity 20pl.

[0028] When fluctuation of the thickness of this thin film was checked by measurement by the laser beam microscope, the difference of a thick part and thin spots was 5% or less, and was uniform. in addition, the ratio of the difference of a thick part and a thin part -- {(thickness of a thick part - thickness of a thin part) -- /-- thickness}x100 (%) of a thin part

It comes out.

[0029] Moreover, when the cathode which consists of aluminum was formed and light was emitted in each pixel, it turned out that green luminescence of homogeneity is obtained within a pixel and the film is formed in homogeneity.

[0030] [Example 2] Silver was contained as a solute and the concentration of a solute did the regurgitation and application of the colloidal solution which is 30wt(s)% according to the circuit pattern (a width of 1 micrometer) of a substrate by the ink jet method.

[0031] Subsequently, the fine structure object formed with the silver coat with a width of face [ as a thin film / of 20 micrometers ] and a thickness of 1 micrometer was acquired by putting in in a chamber the substrate with which the solution for functional coat formation was applied, and decompressing it in 2 seconds from ordinary pressure to 50torr(s) (6650Pa) at a room temperature (20 degrees C). The conditions of an ink jet were made to be the same as that of the example 1 as stated above. When the laser beam microscope estimated thickness fluctuation of the obtained thin film, the difference of a thick part and a thin part was 10%, and was uniform. The uniform electrical property was acquired by [ the ] carrying out a crepuscular-rays exposure.

[0032]

[Effect of the Invention] As explained above, this invention offers the manufacture approach of the thin film as for which the thickness of thin films, such as an organic electroluminescence layer as stated above, a light filter of a color liquid crystal display, and a metal circuit pattern, and the presentation in a display device or a semiconductor device are made to homogeneity, the manufacture approach of the fine structure object equipped with this thin film, and the fine structure object acquired by this.

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[Translation done.]